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Effect of Heating and Cooling Rates on Microstructure of ZnO-CoO-SLS Based Varistor Ceramics

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Abstract: In this research, ZnO-CoO doped with fixed 2 mol% SLS glass based varistor ceramics are produce by using solid state method sintered at 1100˚C for 2 hours. The investigation regarding to the varying heating and cooling rates from 4 to 8˚C/min is discussed. XRD and SEM attached with EDX analyses showed that the main phase was ZnO and Zn_2SiO_4 as the secondary phases distributed at grain boundaries. Average grain size increased from 24.41 to 27.39μm as increase in heating cooling rates from 4 to 6˚C/min. However, the increase of heating cooling rates up to 8˚C/min the average grain size decrease to 25.52μm. The average density, *p* of the sample is decrease from 5.39 to 5.20 g/cm^3 as increase the heating and cooling rates from 4 to 8˚C/min.

Keywords: Heating and cooling rates, average grain size, grain boundaries, SLS glass, varistor

Zinc oxide (ZnO) is a semiconductor material in group of II-VI in periodic table with a minimal bandgap ranging from 3.1 eV to 3.3 eV [1-3]. However, in line with a more in depth research, it was found ZnO has an excellent bandgap around 3.37 eV. ZnO varistor are polycrystalline ceramics consist of ZnO as base materials and additives of metal oxides as dopants; and fabricated through a sintering process. Small amount of additives to be used as dopants is divided into three based on their electrical contribution which are varistor former, varistor enhancer and varistor highlighter [1-2, 4]. Cobalt (Co) ions are act as varistor former and MnO, Cr_2O_3, Sb_2O_3 and lead zinc borosilicate glass are used as varistor enhancer in ZnO based varistor [5] while silicon dioxide acts as grain growth inhibitor [6-7]. The appropriation selection of sintering temperature, sintering time, types of dopants, concentration of dopants and also heating cooling rates is relatively challenging for varistor fabrication.

Several methods of preparing ZnO varistors have been developed by controlling the average grain size of sample hence increase the number of grain boundaries, because the breakdown voltage, V_b of ZnO is proportional to the number of grain boundaries per unit thickness [8-9]. Heating and cooling rates also influence in the performance of varistor. Previous research has varied the heating and cooling rates from 2- 6˚C/min for the preparation of ZnO sample [10-17]. Considerable all the other studies has been focused on the I-V characteristics, So, in this paper, we present the studies of influence heating and cooling rates on ZnO-CoO-SLS glass varistor.

Sample of 96 mol% ZnO+2 mol% CoO+2 mol% SLS glass was prepared by a conventional solid state method. Raw materials were milling with zirconia balls for 24 hours. Polyvinyl alcohols (PVA) 1.75 wt% was added as a binder to avoid cracks in the samples and then granulated by sieving through the 75 μm mesh screen. The sample powder was pressed into pellets with 10 mm diameter and 1 mm in thickness at a pressure of 3 ton/m2. The pellets were sintered at a temperature of 1100 °C in air for 2 hours. They were heated and cooled from the sintering temperature at the range 4-8 °C /min. XRD software X'Pert high score software) was used to analyse the date for crystalline phases. The surface microstructure was examined by a scanning electron microscope (model: JEOL 6400) attached with energy dispersive X-ray (EDX). The density (ρ) of sintered sample was measured by Archimedes method.

Figure 1 shows the density influence by the heating and cooling rates. The higher density of 5.39 g/cm^3 was obtained from pellet with heating and cooling rates at 4˚C/ min. As we increase the heating and cooling rates from 4 to 8 ˚C /min, the average density, *p* decreasing from 5.39 to 5.20g/cm^3. The decrease of the average density shows that high heating cooling rate exhibited low performance of varistor. The high performances of varistor have 95 % of theoretical density or greater [18-19].

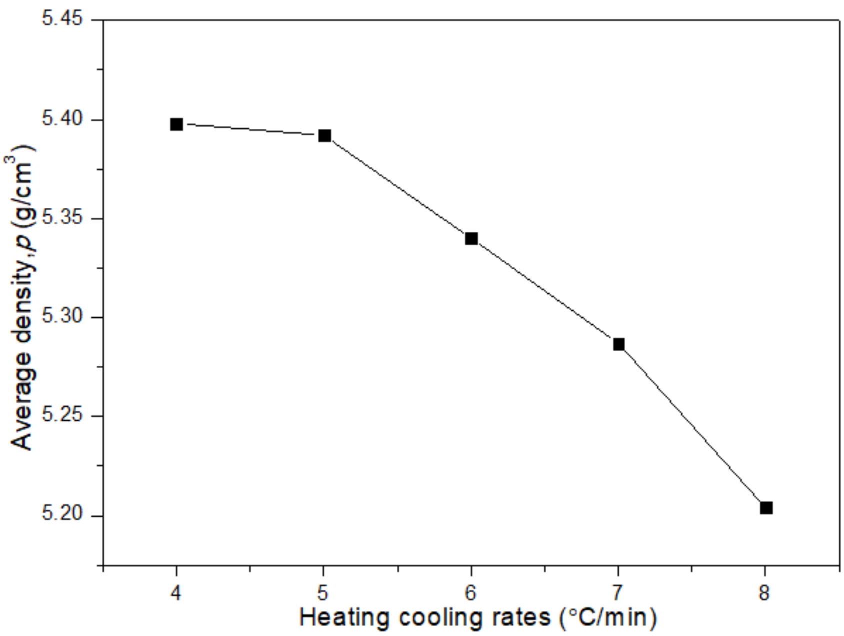

Figure 1: Average density at different heating cooling rates

Figure 2 shows the XRD patterns of the sample sintered at 1100 ˚C where the main and secondary phases of ZnO and Zn_2SiO_4 respectively were observed. There was no Co phase detected as Co successfully diffuse into ZnO lattice sites. Based on SEM micrographs in Figure 3, it shows that the average grain size decreases from 24.41 to 21.60 µm as the heating and cooling rates is increased from 4 to 5 ˚C/ min. The grain size increases to 27.39 µm at heating and cooling rates of 6 ˚C/ min but, slightly decreases to 25.52 µm at 8˚C/ min. This result shows low heating and cooling rates resulting in small average grain size.

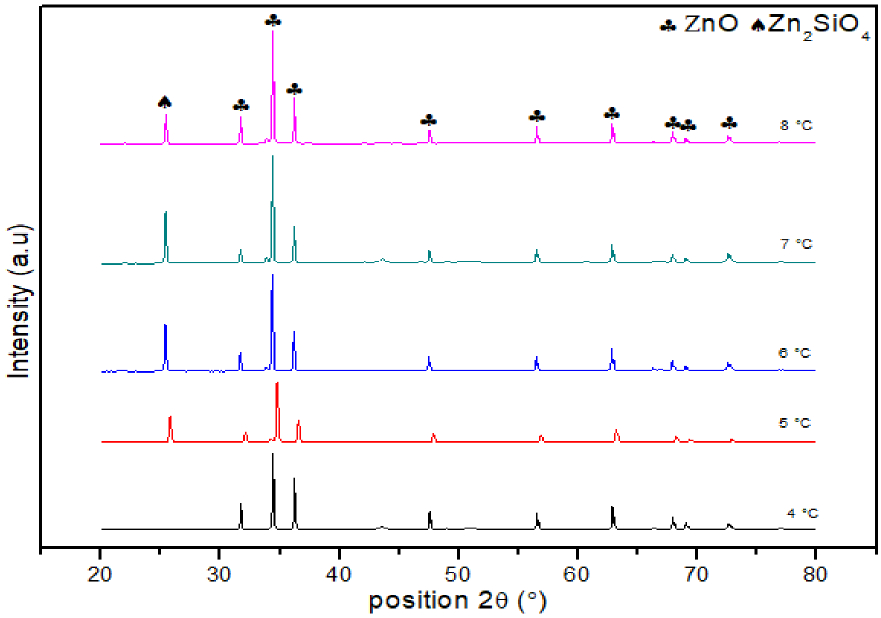

Figure 2: XRD pattern of different heating cooling rates

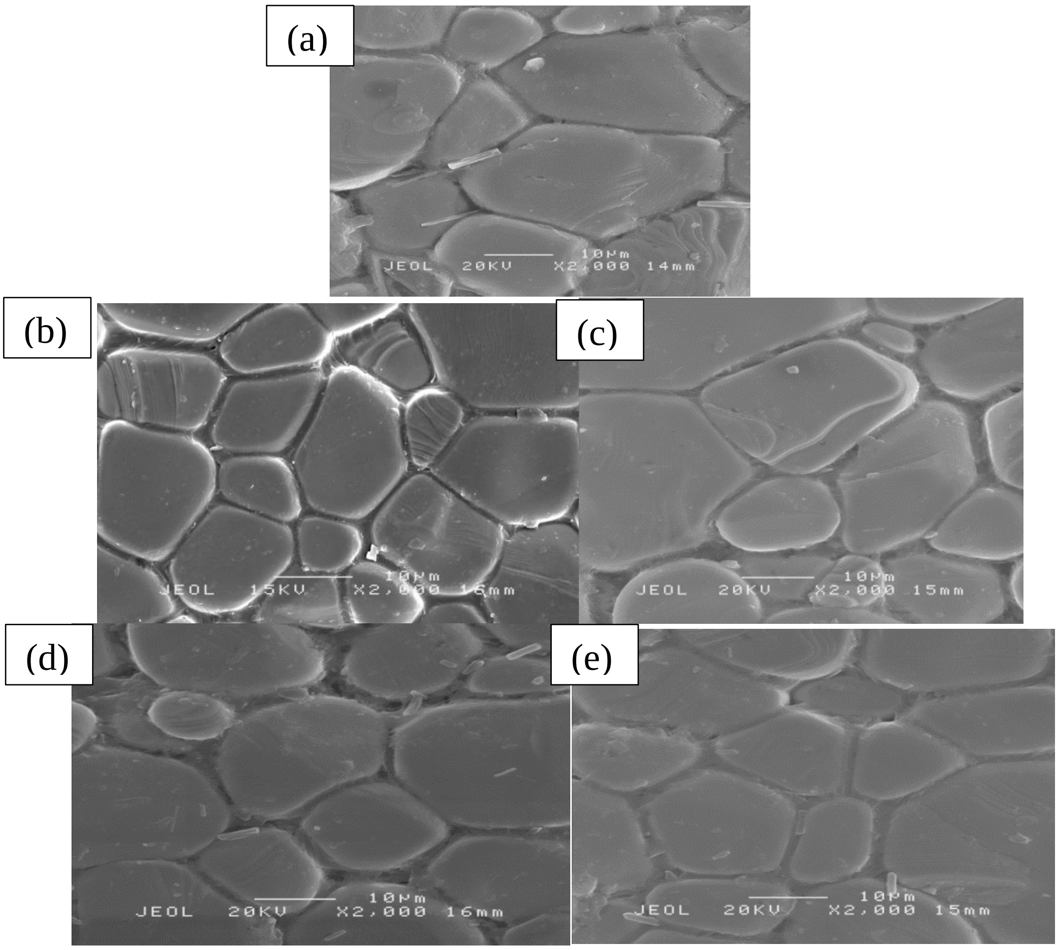

Figure 3: SEM micrograph of different heating cooling rate (a) 4˚C/min, (b) 5˚C/min, (c) 6˚C/min and (d) 7˚C/min, (e) 8˚C/min

Figure 4 shows the EDX spectra for Spectrum 2 and 4. It indicates that the Co and Si are segregated at grain boundaries indicating the secondary phases Zn_2SiO_4 are developed in the ceramics. It was found that Co was present at the interstitial sites at the grain surface due to the substitution of Co is possible in ZnO lattice as the ionic radii of Co ion (0.65Å) are smaller than Zn radii (0.74Å).

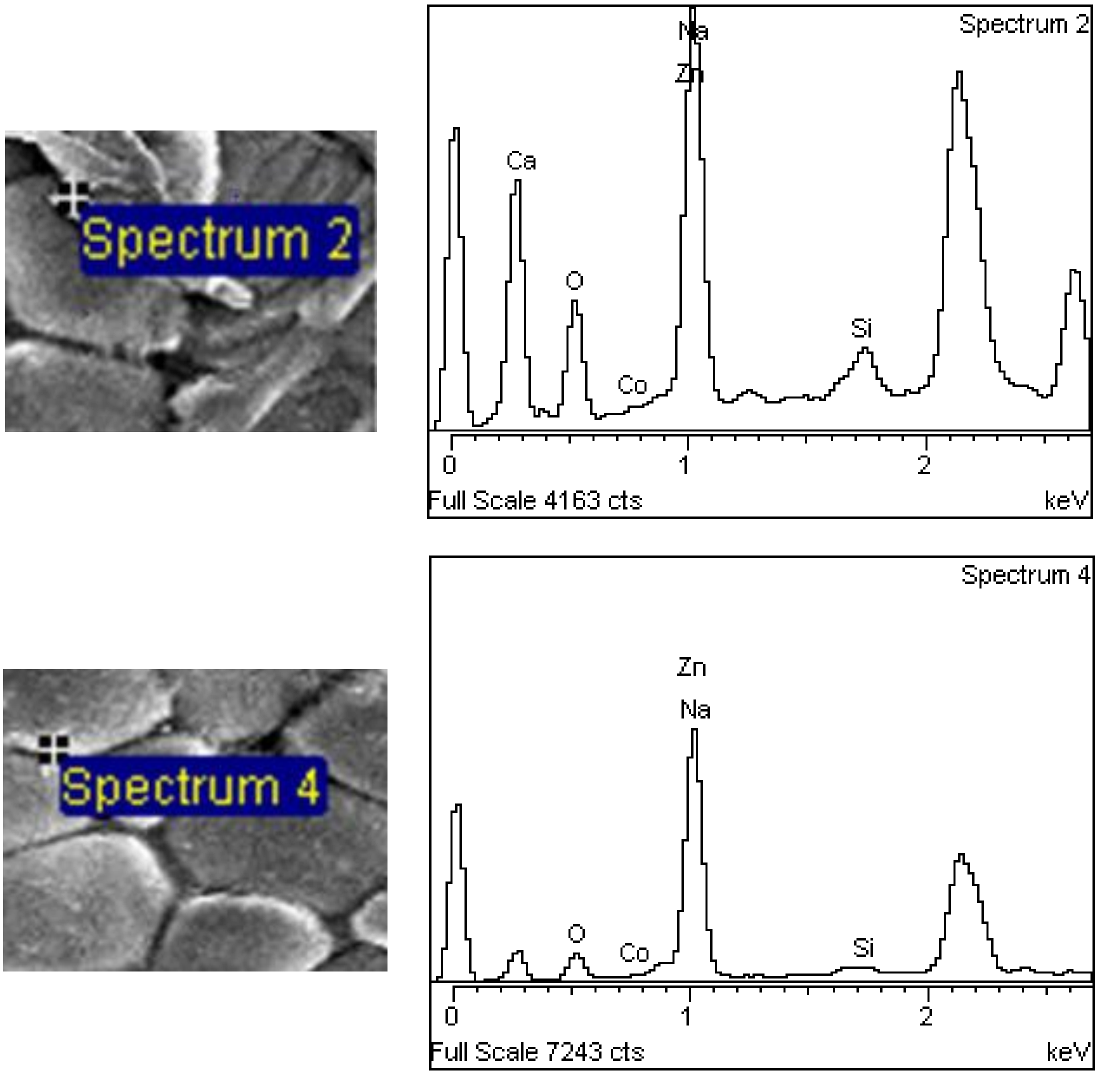

Figure 4: EDX spectra of 4 ˚C/ min heating and cooling rates for spectrum 2 and spectrum 4

In conclusion, the effect of heating and cooling rates on ZnO-CoO-SLS glass was investigated in the range 4 to 8 ˚C / min. The heating and cooling rates influence the microstructure properties of the ceramics. The low heating and cooling rates of 4˚C/min shows the best microstructure properties with highest average density of 5.39 g/cm^3 and small average grain size of 24.41 µm.

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